

# **Studies of Corrosion Resistant Materials being considered for high-level nuclear waste containment in Yucca Mountain Relevant environments**

*R.D. McCright, G. Ilevbare, J. Estill, and R. Rebak*

**U.S. Department of Energy**

Lawrence  
Livermore  
National  
Laboratory

This article was submitted to  
Corrosion National Association of Corrosion Engineers Expo 2002,  
56<sup>th</sup> Annual Conference & Exposition, Denver, CO April 7-11, 2002

**December 9, 2001**

## DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy  
And its contractors in paper from  
U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
Telephone: (865) 576-8401  
Facsimile: (865) 576-5728  
E-mail: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available for the sale to the public from  
U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: (800) 553-6847  
Facsimile: (703) 605-6900  
E-mail: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory  
Technical Information Department's Digital Library  
<http://www.llnl.gov/tid/Library.html>

**STUDIES OF CORROSION RESISTANT MATERIALS BEING CONSIDERED  
FOR HIGH-LEVEL NUCLEAR WASTE CONTAINMENT IN YUCCA  
MOUNTAIN RELEVANT ENVIRONMENTS**

Daniel McCright, Gabriel Ilevbare, John Estill, and Raúl Rebak  
Lawrence Livermore National Laboratory, Livermore, CA 94551

**ABSTRACT**

Containment of spent nuclear fuel and vitrified forms of high level nuclear waste require use of materials that are highly corrosion resistant to all of the anticipated environmental scenarios that can occur in a geological repository. Ni-Cr-Mo Alloy 22 (UNS N60622) is proposed for the corrosion resistant outer barrier of a two-layer waste package container at the potential repository site at Yucca Mountain. A range of water compositions that may contact the outer barrier is under consideration, and a testing program is underway to characterize the forms of corrosion and to quantify the corrosion rates. Results from the testing support models for long term prediction of the performance of the container. Results obtained to date indicate a very low general corrosion rate for Alloy 22 and very high resistance to all forms of localized and environmentally assisted cracking in environments tested to date.

**Keywords:** high level nuclear waste, Ni-Cr-Mo alloys, N60622, Yucca Mountain, J-13 well water, titanium, corrosion resistant alloys, general corrosion, localized corrosion, stress corrosion cracking, microbiologically influenced corrosion, physical metallurgy, process metallurgy

## INTRODUCTION

The suitability of the Yucca Mountain is under investigation as the potential site for geological disposal of commercial nuclear spent fuel and some other forms of high-level nuclear waste in the United States. The site is located about 120 km northwest of Las Vegas in the state of Nevada on federally-owned land. The repository for the waste disposal would be constructed in a layer of tuff rock, known as the Topopah Spring member, at a depth approximately 300 meters below the earth's surface and about 300 m above the permanent water table at this location. The Yucca Mountain site is unique among potential repository sites under consideration in the different waste disposal programs throughout the world, since the waste would be emplaced in the unsaturated zone above the water table and in an environment that is fundamentally oxidizing in nature.

The purpose of this paper is to describe briefly the design of the waste package and the behavior of the proposed materials for nuclear waste containment. Because the long-term corrosion of the waste package materials is the paramount performance concern for containment of the waste package, an analysis of the expected corrosion performance occupies the main part of this paper. Last, the corrosion testing activities and modeling of the long term behavior based on results of the testing are discussed. The testing and modeling are on-going efforts, and it is expected that these activities will proceed for several more years into the future.

The overall strategy in isolating high-level nuclear waste is to make use of the natural barriers present in the host geology along with the construction of a series of engineered barriers. The waste package is an important component of the engineered barrier system. If the Yucca Mountain site is found suitable and recommended for a geological repository, two generic types of waste are planned for disposal there: (1) spent nuclear fuel from the commercial power reactors and from special DOE reactors. This waste is currently stored in many locations in the country. Assemblies of spent nuclear fuel would be delivered to the Yucca Mountain site, "as-is" from these storage locations. (2) reprocessed waste from defense programs and from commercial power reactors. At a few sites in the country, this reprocessed waste is converted into a borosilicate glass that is poured and molded in stainless steel canisters. These canisters would then be delivered to the Yucca Mountain site.

## WASTE PACKAGE DESIGN AND MATERIALS

### *Waste Package Design and Repository Configuration*

The current waste package design consists of two concentric metal containers. The outer container would be made of Alloy 22, a Cr-Ni-Mo alloy (UNS N06022), which is among the most corrosion resistant of all engineering materials. The purpose of this outer container is to provide corrosion protection as the primary containment barrier. The thickness of this container is 20 mm. The inner container would be made of a 50-mm thick, special nuclear grade of Type 36L stainless steel (UNS S31603). However, its



intended purpose is to provide additional bulk and mechanical strength. It is not considered as a containment barrier. In order to provide even greater performance, it is proposed to emplace a titanium drip shield around the waste package to intercept any falling water from the repository drift wall. The drip shield will be fabricated principally from Grade 7 Ti (UNS R52400), which contains a small addition of palladium to provide a very high degree of corrosion resistance. While both Ti-Grade 7 and Alloy 22 are extremely corrosion resistant over a wide range of environments, the strategy here is that whatever environmental/metallurgical factor might fail the Ti would not fail the Alloy 22 outer barrier.

A schematic of waste package emplacement in a repository drift is shown in Figure 1. The waste package rests on a platform fabricated from Alloy 22 to avoid galvanic effects in this region. The platform in turn sits on a steel frame and crushed gravel invert. The drift wall is lined with either concrete or steel. In the present plan, waste packages would be fabricated, filled with waste, and emplaced over a 30-year period. The Ti drip shield would be installed some time after waste package emplacement. The drifts would be ventilated, by force or by natural means for many years. A backfill consisting of the crushed tuff rock excavated during repository construction could then be emplaced over the whole metallic structure. Backfilling the repository drifts is an option that would remain for a future decision.

The current plan is to co-mingle the different kinds of waste packages in the drift in order to create a reasonably constant thermal output in each drift. Large waste packages are planned in which several commercial spent nuclear fuel assemblies are encanistered in the same waste package. Similarly, multiple canisters of reprocessed waste are encanistered in the same waste package. Figure 2 illustrates how these different types of waste packages are co-mingled and emplaced in a repository drift. In general, the waste packages have a common diameter (1.8 m), and the length varies according to the type of waste (roughly 3.6 m for the reprocessed waste to 5.7 m for most of the spent nuclear fuel waste packages). However, there are several specific designs necessitated by accommodating the different dimensions of spent fuel used in the various commercial reactors throughout the USA.

### ***Waste Package Containment Material***

Alloy 22, perhaps better known under one of its trade names, Hastelloy C-22, was developed for outstanding corrosion resistance to a wide variety of chemical environments. It is related to a number of "C" types of alloys, all with approximately 60% Ni and containing different amounts of Cr and Mo, and sometimes other alloying elements. These elements impart a great deal of resistance to localized forms of corrosion and environmentally accelerated cracking. The alloy is used extensively in the chemical process industry and in pollution abatement applications. The composition of Alloy 22 is given in Table 1. Most of this paper is devoted to discussion of potential corrosion problems with Alloy 22 and the testing program that is underway to resolve those problems and to provide the experimental inputs into the performance modeling of the behavior of this material. Some work on titanium is underway, but the testing

program on this material is not as advanced as that on Alloy 22. In fact, much of the work that has been performed on projecting the corrosion performance of Alloy 22 has in fact been performed *assuming* that the Ti drip shield is *not in place*. Thus, it is assumed that the aqueous environment resulting from drips issuing from the repository drift wall contacts the waste package directly.

In addition to Alloy C-22 (UNS N06022), a limited amount of testing on some of the other C-type alloys is being performed. These alloys include Alloy C-4 (UNS N06455), Alloy C-276 (N10276), Alloy 59 (UNS N06059), and Alloy 686 (UNS N60686). These are being tested as potential alternative materials in case a problem is found with Alloy C-22 or as comparative materials. Also, other grades of titanium are under test. These are listed in Table 1.

### ***Container fabrication***

The current plan is to fabricate the waste package containers from rolled and welded plate material. For the Alloy 22 outer container, two heats of material are required for the body of the container, resulting in a number of assembly welds. A bottom lid is then welded onto the container body. All of these assembly welds can be solution annealed to relieve residual stress and eliminate segregation of alloying elements in the weld region. However, post-weld treatments on the top lid are more limited because these must be performed after the waste is placed in the waste package. This requires the final closure welds for each container to be performed in a hot cell facility and limits the times/temperatures of any post-weld treatments because to potential damage to the waste form. Because of the strong interaction between corrosion performance and the metallurgical structure in and around the weld, this subject will be discussed later on in the paper.

## **ENVIRONMENTS ON THE WASTE PACKAGE SURFACE**

### ***Types of Water***

The ground waters that are associated with Yucca Mountain have been well characterized. [1] In particular, most emphasis has been placed on the composition of water from the J-13 well as being representative of water that would originate from atmospheric precipitation and would infiltrate along fractures in the various tuff layers including the Topopah Spring layer in which the repository would be constructed. However, over the years other types of waters have been considered in the analysis of environments relevant to waste package (and drip shield) performance. One such type of water is pore water that would be formed in an upper rock stratum and then find its way also along the fractures leading into the repository drifts. Regardless of the water source, the significant feature of any of the waters is the evaporative concentration effects that occur when the water, dripping from the drift wall, strikes the warmer waste package container surface. Repeated dripping will cause build-up of the salts evaporated from the water.

Many of the salts associated with the Yucca Mountain waters are hygroscopic in nature. As the temperature decreases, the relative humidity increases in the atmosphere around the container. Eventually a point is reached where an aqueous solution can be maintained because the deliquescence point of the salt mixture (in terms of temperature and relative humidity at that temperature) lies at or below the temperature on the surface of the container. (Much like moisture condenses on an object when the atmospheric temperature is at or below the dew point). An aqueous solution is then formed around the deposited salt. Further dripping of water onto the surface will add more liquid. Solutions with relatively high concentrations of salts in the water are therefore the most representative of *aqueous* environmental conditions. Nevertheless, the climate at Yucca Mountain is dry and water quantities reaching the waste package surface are limited. However, the performance of the material under aqueous conditions is by far more limiting than those under dry conditions (the dry oxidation rate of Alloy 22 is negligible) and therefore receives the most attention in the testing and modeling work.

While a detailed discussion of the geochemistry and hydrology of the Yucca Mountain site is beyond the scope of this paper, from the point of view of the waste package performance, the fundamental consideration is that the testing and modeling effort cover the range of environmental conditions. In fact, a large effort has been performed on characterizing what are termed bounding environments. The infiltration water and the pore water reflect two rather different water types:

1. The infiltration water is a bicarbonate dominated type of water with significant concentrations of sulfate, nitrate, and chloride. Alkali (Na and K) cations dominate over alkaline earth (Ca and Mg). The water also contains some fluoride and is saturated in silica. Its pH is just slightly alkaline in the dilute water, but with concentration of its salts, the pH is raised into the 10-11 range, mainly because of the bicarbonate/carbonate buffering effect.
2. The pore water is characterized by the absence of any carbonate species. It contains significant amounts of sulfate, nitrate, and chloride, but the alkaline earth cations dominate over the alkali cations. It is slightly acidic when diluted but when concentrated, it remains near neutral, since there is no carbonate to alkalize the solution.

In both cases, a high concentration of nitrate develops. The lack of macrobiological activity (i.e. plant life) is probably responsible for the high levels in the dilute waters. Owing to the high solubilities of nitrates, evaporative concentration leads to high nitrate concentrations. This is significant with respect to corrosion performance because the nitrate is an important factor in establishing the overall redox conditions. Nitrate ion also demonstrates inhibiting effects in localized corrosion initiation and probably stress corrosion, too; thus mitigating the effects of aggressive ions, chlorides and fluorides. Other ions in solution also seem to show mitigating or inhibiting effects on localized corrosion. In addition to nitrate, the aqueous environment is saturated in oxygen, because the highly fractured rock permits communication with the atmosphere. An exception to the dominant oxidizing conditions expected on the waste package container surface

would occur in crevices (such as the point where the waste package rests on the support structure shown in Figure 1), and under deposits and under biofilms.

### ***Ventilation and Dust***

The repository drifts will be ventilated for some time after waste package emplacement, either by forced or natural means. Ventilation will bring in "foreign materials" in dusts, including silica from the terrain, organic material, microbe spores, and various salts – many of the same constituents found in the infiltration and pore waters. The main issues with the dust deposits are the hygroscopic properties of the constituents and whether aqueous conditions would develop at some early time. The implications of the properties of the dust constituents on potential corrosion effects are being evaluated, but have not yet specifically been incorporated into the testing program. Much of the range in the geochemistry of the water is expected to cover this, with perhaps some justification for changing the ionic ratios of some of the water constituents to cover the possible ranges of these species in the dust.

### ***Temperatures***

The peak surface temperature that develops on the waste package container surface depends strongly on how closely the waste packages are placed in the repository drift. Historically, the strategy of the repository design configuration is to elevate the waste package container surface above the boiling point to keep the surface dry and defer any aqueous corrosion effects. In the present design, a maximum peak surface temperature of 160 C will occur on the waste packages once the repository is closed. The temperature decays slowly requiring hundreds of years until temperatures in the boiling range (considering the deliquescent properties of the solutes) are attained. However, more recently the project has considered an option for keeping the peak surface temperatures at a much lower value (~85 C) by using a less compact arrangement of the waste packages in the repository. However, this option means that aqueous corrosion conditions will be encountered at a much earlier time after waste emplacement and puts additional emphasis on the performance of the waste package.

### ***Microbial Effects***

There is abundance of microbiological life in the repository setting. Microbial activity is expected once sufficient moisture is present. However, the main concern is their effect on changes in the water chemistry. For instance, types of microbes (bacteria and fungi) producing acids, microbes oxidizing iron (steel is used in the repository construction), microbes producing strongly reducing conditions (sulfate reducers) could lead to scenarios that might be damaging to Alloy 22. Since microbes often form localized colonies and consortia of different types on metal surfaces, the chemical conditions can change radically from point to point. This is further discussed below since it may contribute the possibility of aggressive conditions and this has important implications on the expected corrosion performance of Alloy 22.

### ***Radiolytic Effects***

One further environmental effect is the influence of radiolysis on changes in the water chemistry. The relatively thick two-barrier design (5 cm + 2 cm) attenuates the gamma radiation field by ~ 3 orders of magnitude. The major gamma producing isotopes have half-lives around 30 years, thus each 100 years in the repository reduces the radiation field by another order of magnitude. The main concern with radiolysis is the combination of a significant gamma field with aqueous conditions, certainly more of an issue if a lower thermal load of waste packages is used in the repository. On the other hand, a moderate radiolysis effect may be beneficial in equilibrating redox conditions between creviced and non-creviced areas.

### ***Path Forward***

In organizing the testing and modeling approaches in evaluating Alloy 22, both representative environmental conditions are used as well as aggressive conditions. The aggressive conditions are often beyond conditions that bound the expected environmental regions (pH, temperature, ionic strength, ratios of various ions, etc). This is especially necessary for a corrosion resistant material where the amount of corrosion damage measurable in real laboratory time (up to several years) is below detection. While such null tests are important for long term performance confirmation, models for performance cannot be based on such tests alone. Testing under the more extreme conditions and then extrapolating those results to the expected conditions is an approach that will lead to more defensible models of the expected cases.

## **POTENTIAL CORROSION PROBLEMS WITH ALLOY 22**

Despite the reputed excellent corrosion resistance of Alloy 22, it is necessary to demonstrate that this behavior is relevant to Yucca Mountain conditions. The overall strategy has been to show that a low rate of passive general corrosion is the only operative corrosion mode over the range of environments likely to contact the container surface. Localized forms of corrosion (pitting, crevice, intergranular – including microbiologically induced contributions to localized corrosion) and environmentally assisted forms of cracking (stress corrosion cracking and hydrogen induced cracking) must be shown to be low probability events. Furthermore, if these forms of corrosion are initiated, then it must be shown that propagation is slow and tends to stifle with time. In order to carry out this large amount of work, a comprehensive testing and modeling program has been initiated.

### ***Performance Models***

A model for the overall, or integrated, performance of the waste package container is a composite of several smaller individual models that are, in turn, based on the response of the material to various forms of corrosion. These models include a number of factors dealing with the environments in the drift and metallurgical structures resulting from processes used for fabricating and welding the metal container. Figure 3 is a chart

illustrating the compilation of individual models. Inputs into the model include the drift environment (upper left box of chart) that becomes modified in composition by contact with the hot container surface (box below), whose temperature is determined largely by the radioactive decay heat output of the package. The diamond shaped box below this indicates a critical juncture. If the environment is dry (relative humidity below critical amount to sustain moisture), low temperature oxidation is the only degradation mode, and a very simple low-temperature dry oxidation model is operable:

Aqueous conditions occur if the relative humidity levels is above the critical level, taking into account the deliquescence properties of salts in lowering the critical humidity level. The box in the center of chart shows the major considerations for the box labeled waste package environment, namely the chemistry of the water, any microbiological activity in this water, and whether there are crevice conditions on the waste package container surface. The diamond below this box shows another juncture, this one based on the electrochemical corrosion potential that develops on the waste package surface. If this potential is below a critical value (discussed below), then general corrosion (which would be low due to the protective quality of the passive layer) is the operating mode. If the corrosion potential is above the critical potential, some breakdown of the passive film occurs, and much more rapid localized corrosion takes place. Actually, there are a number of different critical potentials corresponding to initiation and propagation of localized corrosion and whether the attack occurs within a crevice or on the boldly exposed (non-crevice) surface, which corresponds to pitting attack.

There is a line drawn directly from the waste package environment box to the localized corrosion box without passing through the critical potential criterion. This was done because the microbiological considerations do not lend themselves to the same experimental techniques (polarizing the metal, this is discussed later), but in reality there is a similar criterion – a critical chemistry around the microbe colonies to initiate corrosion in this location.

The metallurgical condition plays an important role in the performance (boxes on the right side of the chart). The alloying elements in Alloy 22 that provide so much of the corrosion resistance can, in some instances, form phases at high temperatures that are brittle. These phases are rich in Cr, Mo, and W, and can deplete local areas of these elements making them less corrosion resistant. Work is proceeding on projecting the phase stability at the more moderate temperatures relevant to the repository. The processes for fabricating and welding the container also modify the structure and welding modifies the local composition of the alloy. As indicated on the chart in Figure 3, these effects influence the critical potentials and therefore the tendency toward localized forms of corrosion.

The larger effect of the metallurgical variables arising from the processes for fabricating and welding the container is on the stress corrosion cracking (SCC) behavior. The residual stresses remaining after the final closure weld is made and flaw sizes that would be present, particularly in the welded areas, obviously affect the stress and stress intensity in this area. For this reason, stress mitigation treatments are being studied to lessen the

stress, bearing in mind that performing these treatments in a hot cell and on a container filled with waste imposes many restrictions on the processes. One promising stress mitigation technique is laser peening, in which a compressive stress is put onto the surface by the shock wave produced by a laser impulse. SCC does not initiate under compressive stress, the laser peening can produce about a compressive layer to some depth (~ 3 mm) in the metal, and this process can be performed within the restraints of the hot cell.

Stress corrosion cracking models are based on either a critical stress or a critical stress intensity to initiate a crack. Experimental work is underway (described later) for provide data for these models. The right side of the chart shows the interplay between major inputs into these models, including analyses of the physical metallurgy, the process metallurgy, and fabrication issues. The environmental inputs are also a part of the SCC models, as indicates by the lines that join those boxes.

The composite of individual models produces the overall model for the performance of the waste package, as indicated in the bottom box of Figure 3. The same rationale will be used to produce a parallel and comparative model for the drip shield, but this is less further developed.

A testing program is in place to provide experimental data for these models. The program is divided into the following parts:

1. Studies of the environment on the waste package surface
2. General corrosion studies
3. Localized corrosion studies
4. Microbiologically influenced corrosion studies
5. Passive film stability studies
6. Stress corrosion cracking studies
7. Metallurgical phase stability studies
8. Process metallurgy influences on corrosion behavior

These parts are discussed below:

### ***Studies of the environment on the waste package surface***

Different environmental scenarios are under study to describe the ranges of aqueous environments that can contact the waste package and drip shield surfaces. Waters of different types can arise by “chemical divides” of the initial dilute water as the various species concentrate on the warm or hot metal surface. The chemical divide is determined by the relative amounts of calcium, magnesium, and carbonate species in the water. If the carbonate (either as  $\text{HCO}_3^-$  or  $\text{CO}_3^{=}$ , according to the initial pH) exceeds the Ca level and the Mg level, then the resulting water will become higher in pH. The perched waters and infiltrating waters that eventually accumulate in the saturated zone at Yucca Mountain fall into this category. This is expected to be the dominant aqueous environment at the repository horizon. However, another type of scenario is the situation

where the alkaline earth (Ca and Mg) component dominates over the carbonate component. This action results in a near-neutral water after evaporation-concentration of species, but in the latter stages, the excess Ca precipitates out the sulfates, resulting in the relative increase in chloride concentration. The pore waters at Yucca Mountain are of this type of water. The main concern with this type of water is the resulting balance of aggressive chloride ion to the inhibiting oxyanions – nitrate, sulfate, carbonate, silicate, and how these waters could create a more corrosive condition. Fortunately, the high solubility of nitrate counteracts the increase in chloride concentration.

The possibilities of concentrating the minor constituents in the rocks and waters associated with the site have been raised. In particular, such heavy metals as lead, mercury, and arsenic in very high concentrations can cause localized corrosion and stress corrosion on Alloy C-22. Typically, their concentrations in Yucca Mountain groundwaters are on the order of a few ppb. Nevertheless, evaluation of their role at Yucca Mountain suggests that they cannot attain high concentration levels because of so many other interactions with other chemical species that would precipitate them before making contact with the waste package container surface.

As a result of the environmental scenario analyses, several reference waters have been developed over the years for conducting corrosion tests. These waters represent bounding conditions. The compositions of these waters are listed in Table 2. A more detailed explanation of their origins is available [2]. These waters are all simulated; that is, they are made up by adding different chemicals (e.g. NaCl, KNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>) to distilled water according to formulas to yield the target compositions in Table 2.

### ***General Corrosion Studies***

One of the strategies of the Yucca Mountain materials work is to show that forms of corrosion other than general corrosion are highly unlikely to initiate, and even if they did initiate, that their continued propagation would be stifled. That said, general corrosion or more correctly corrosion through passive dissolution is the default corrosion mode, whose very slow kinetics would ensure a long-lived waste package container. General corrosion rates have been measured and are continuing to be measured. A long term corrosion test facility has been in operation for more than five years, in which coupons of the candidate materials for waste package and drip shield materials, in different configurations, are exposed to several of the waters listed in Table 2.

The most recent determination of the general corrosion rates of Alloy 22 was made in 1999 after 2 years of exposure to the test solutions. The next determination is scheduled for early 2002, which will mark the fifth year of exposure for the Ni-base and Ti-base alloys. Results obtained after the 2-yr exposure have been published and discussed [3, 4]. A summary of these results comprises Table 3. It is noted that the general corrosion rate is decreasing with exposure time. Also, there was no noted difference in rates obtained in the range of water compositions and temperatures tested. If one were to take a grand average of all the results so far, the corrosion rate of Alloy 22 is around 20 nanometers/year.



These results are not surprising. For one thing, Alloy 22 is expected to be passive over this range of pH (2.8 to 10.5 – these are the actual measured pHs of the SAW and SCW solutions after 2 years ), temperature (60-90 C), and ionic strength (from ~ 70 ppm chloride to ~ 40,000 ppm chloride).and water compositions in Table 2. Any differences in corrosion rates would be small. Another factor is that the weight loss method used in these investigations is not very sensitive to such low corrosion rates. The error in weighing is of the same order of magnitude as the amount of weight loss. However, as the exposure time increases, the weighing error will become less important. Another approach is to emplace specimens with a much larger surface area to volume ratio than the present coupons (nominally 5 cm length x 2.5 cm width x 1.6 mm thick). Planned future work is to explore other test methods for measuring the general corrosion rate, such as electrochemically-based linear polarization, which can be used on an intermittent basis to measure corrosion rates in situ while a specimen is exposed for a long duration. It is important that general corrosion rates be measured over long time periods to allow passive films to form and grow in the test environment, conditions that would simulate those occurring on the container surface. It will be interesting to note if these same observations will hold true for results obtained after the 5-yr exposure.

### ***Localized Corrosion Studies***

As shown in Figure 3, the criterion for initiating localized attack is the critical potential above the corrosion potential or open circuit potential. Alloy 22 is extremely resistant to localized corrosion in a wide range of chemical environments. Indeed, the alloy only becomes susceptible in such media as hydrofluoric acid or one of the acid, high chloride, oxidizing environments such as the “green death” or “yellow death” solutions [5]. Crevice corrosion is more of a concern than pitting corrosion for Alloy 22. Traditionally, critical potentials are measured by cyclic polarization of susceptible materials, first scanning potential in the anodic or oxidizing direction until after a large increase in current from the passive current is noted, corresponding to breakdown. Then, the potential is scanned in the reverse direction and the potential at which passivity is restored corresponds to repassivation. For a highly resistant material, like Alloy 22, it is difficult to measure an electrochemical potential corresponding to passive film breakdown because these breakdown potentials are usually more anodic than the oxygen evolution reaction. The increasing current corresponding to oxygen evolution masks whatever current would correspond to passive film breakdown. Eventually, one would expect to observe some partial dissolution of the alloy as the potential for oxidation of Cr+3 (dominant species in the oxide film) to soluble Cr+6. Possible oxidation of Mo species is another transpassive reaction that may also contribute to dissolution especially at the higher values of pH. Conducting potentiostatic experiments in this range of potentials and then performing some type of analysis on the corrosion products is a way of determining which reactions are proceeding in this region.

A large number of cyclic polarization tests have been conducted in the same types of waters used in the long term corrosion immersion tests, and have been reported [3]. No discernible localized attack has been noted on any of the Alloy 22 specimens exposed in

the immersion tests. In this same reference, measurements of the corrosion potential and what are called the critical potentials show a comfortable margin between the two values so that there is no expectation of localized attack. However, work is continuing since recently some increase in the corrosion potential over time has been noted in the acidified concentrated water (SAW) at pH 2.8. This is the subject of another paper in this symposium [5].

It is possible to initiate crevice attack in Alloy 22, but the environmental circumstances for doing this are extreme. Specimens of the material maintained in a 4M sodium chloride only solution at 1000 C and polarized to +350 mV (Ag/AgCl saturated Cl scale) for 2 hours showed attack in the intentionally creviced area of the specimen. This potential is well above the corrosion potential in this environment (-450 mV). When inhibiting ions, particularly nitrate, were introduced into the test environment, no localized attack was observed even at comparable highly anodic potentials. Work is continuing to better indicate the regions of susceptibility for this material. Of particular concern is an environment issuing from evaporative concentration of the pore water composition, since this water would be "rich" in calcium chloride. Because  $\text{CaCl}_2$  becomes exceedingly soluble at high temperatures (~ 16 M at 120 C) and mildly acidic, it may be aggressive toward Alloy 22. However, the nitrate ion is present in pore waters and is also exceedingly soluble and is expected to nullify the aggressiveness of the chloride, but experiments to prove this statement are still on-going.

### ***Microbiologically Influenced Corrosion (MIC) Studies***

Studies on MIC contribute to the waste package surface environmental studies and to the localized corrosion studies. To date, the project has not determined a specific worst-case MIC environment, but a combination of acid producers, iron oxidizers, and sulfate reducers have only indicated a superficial increase in the general corrosion rate over that observed under the same starting environment but sterile of microbiological activity. Thus, the MIC contribution is handled as a multiplier to the overall general corrosion rate, a factor of 2.5 as determined by linear polarization measurements in 100 X J-13 water.[3]

Work is continuing, because if MIC were an important degradation mode, it would be expected to occur locally at a much higher rate. Sulfate reducing bacteria would appear to be one of the most aggressive toward Alloy 22 because some of the reduced sulfur states (sulfite, thiosulfate, and sulfide) are particularly corrosive to at least some Ni-containing alloys.

### ***Passive Film Studies***

The high resistance of Alloy 22 to localized corrosion and to stress corrosion is the high stability of the passive film over a wide range of temperature and chemical conditions. The combination of nickel, chromium, and molybdenum in the alloy and the juxtaposition of the stability regions for the individual oxides (Ni in basic solutions, Cr and Mo in more acidic solutions) suggests a synergism. The combined oxide, whether it

is a mixed oxide or a spinel structure, is more stable than the oxides of the individual component. Activities are underway to calculate potential-pH stability (Pourbaix) diagrams for the alloy, including the significant multi-component chemical species in the environment. A number of surface analytical techniques are being used to determine the chemical and structural properties of the film formed under various conditions for different times to see if these characterizations approach the thermodynamic predictions.

### ***Stress Corrosion Cracking Studies***

While Alloy 22 would be predicted to be highly resistant to SCC over the range of expected water chemistries and temperatures, the high level of residual stress in the final closure weld and any possibility of a chloride dominant environments gives pause. Assembly welds made during the container fabrication are expected to be solution annealed to remove residual stress and restore the alloy homogeneity in the welded region. This will help to mitigate any possible SCC initiation. Nevertheless, experimental work is underway to discern any susceptibility of the material to SCC and to determine where the conditions causing the attack could occur in the repository setting. To date, examination of around 100 U-bend specimens exposed for up to two years in the bounding water chemistries of the long term corrosion test have not revealed any crack initiation. No SCC has developed on slow strain rate tests exposed to a wide variety of repository relevant environments, even when these environments are polarized anodically. The only case where a slow strain rate test showed substantial loss of mechanical properties was in a 4M chloride-only solution, polarized anodically, but examination of the post-test specimen surface indicated enhanced localized corrosion in a creviced area under the polymeric Halite coating. These environmental conditions were similar to those causing crevice attack and discussed above under localized corrosion.

Longer term SCC tests are being performed by exposure of pre-cracked (wedge open loaded) and smooth (constant tensile load) specimens in the load in the long term corrosion testing facility (environments listed in Table 2) and in selected more aggressive environments. Also, SCC crack propagation studies are underway using reversing DC measurements to monitor crack extension. Crack propagation progresses under tensile/tensile cyclic load, and as expected the crack growth rate decreases as the frequency of the cyclic loading decreases.

### ***Physical Metallurgy Studies***

The alloy additions of bcc, Cr, Mo, and W, appear to promote the formation of tetragonally compact structures, such as sigma, mu, and P phases at high temperatures (>700 C). These phases reduce the mechanical properties of Alloy 22 if present in significant amounts and locally may denude the regions surrounding the precipitation of the secondary phase of Cr, Mo, and W – elements that promote the corrosion resistance of the alloy. The concern was whether these phases could form at much lower temperatures (relevant to the repository) but at very long times. In the base metal, this appears very unlikely, but work is continued to ascertain if the welded regions would be more susceptible. An ordered phase forms at somewhat lower temperatures, and

formation of this phase may be encountered during the long times at moderately low temperatures.

Calculations of the thermodynamic stability of the different phases have been made, as well as the time-temperature-transformation diagrams for the kinetics of these reactions. These calculations are now being compared to experimental data [7]. In some cases, specimens have been thermally aged for several years. To date, the phase stability calculations and the TTT calculations indicate no expectation of the presence of TPC phases at repository relevant temperatures. However, these calculations need to be performed over the entire compositional range that would develop in the welded areas.

The work in this area of investigation also produces test specimens for corrosion testing. These specimens have different thermal aging treatments, some of them quite prolonged, to bring out the different microstructural features. Another paper at this symposium addresses corrosion concerns with microstructures produced by long term exposure to high temperatures [8]. These can be considered as bounding metallurgical cases, analogous to the bounding environmental cases described earlier in this paper. This work is continuing in order to include the full matrix of metallurgical conditions, including aging at a range of temperatures and times to favor formation of the ordered structure and the tetragonally compact structures. Also, welded microstructures with and without thermal aging and cold-worked microstructures are being prepared for testing.

#### ***Process metallurgy influences on corrosion behavior***

Work in this area of investigation is focused on producing typical and bounding metallurgical structures that are used for corrosion testing, parallel to the above area on physical metallurgy. Prototype fabrications of waste package sections (full diameter and approximately ¼ length) have been made and are being fabricated into test specimens. Stress mitigation processes around the final closure weld (top lid onto the container body, filled with the waste form) have been proposed to alleviate susceptibility to stress corrosion cracking. The two processes under active consideration are laser peening and induction annealing. Laser peening produces a compressive stress layer on the welded waste package surface, and with optimization of the process, this layer achieves ~ 3 mm in depth. Induction annealing is local heating of the weld region along with rapid cooling to relieve the stress and to form a more favorable microstructure. This process is also being optimized.

### **CONCLUSIONS AND FORECAST**

To date, the corrosion test results and analysis of these toward long-term performance suggest that Alloy 22 (UNS N06022) is a good choice of material for the corrosion-resistant outer barrier material of the waste package. However, much more work is needed to make a demonstrable case that this material will have sufficient corrosion resistance for all the *reasonable* “what-if” cases. This paper presented an outline of the corrosion concerns and the testing program to address those concerns. Resistance to localized corrosion is the most important current concern, but resistance to stress

corrosion cracking is also important. The range of environmental changes that microbial activity can generate also receives a good deal of attention. While testing under environmental conditions that are representative of the waters eventually contacting the metal container has thus far indicated a very low general corrosion rate and absence of other forms of corrosion, current and future efforts are directed toward more aggressive environments so that localized forms of corrosion are intentionally initiated. Then, these corrosion rates can be extrapolated to the more representative conditions to confirm that the "null results" are indeed valid.

## ACKNOWLEDGMENTS

This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract number W-7405-Eng-48. The work was supported by the Yucca Mountain Site Characterization Project, which is part of the DOE Office of Civilian Radioactive Waste Management.

## REFERENCES

1. J. E. Harrar, J. F. Carley, W. F. Isherwood, and E. Raber, Report on the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations, LLNL UCID Report 21867 (University of California, January 1990)
2. G. E. Gdowski, Environment on the Waste Package Outer Barrier and Drip Shield, Report ANL-EBS-MD-000001 (Yucca Mountain Project, December 2000)
3. J. C. Farmer and R. D. McCright, General Corrosion and Localized Corrosion of Waste Package Outer Barrier, Report ANL-EBS-MD-000003 (Yucca Mountain Project, January 2000)
4. J. C. Farmer and R. D. McCright, , General Corrosion and Localized Corrosion of Waste Package Outer Barrier, Proceedings, 2000 American Society of Mechanical Engineers Pressure Vessel and Piping Conference (Seattle, WA, ASME, July 2000)
5. R. B. Rebak, N. E. Croon, J. P. Cotner, P. Crook, in Passivity and Localized Corrosion, vol. PV 99-27 (Pennington, NJ: The Electrochemical Society, 1999)
6. G. O. Ilevbare, T. Lian, and J. C. Farmer, Environmental Considerations in the Studies of Corrosion Resistant Alloys for High-Level Radioactive Waste Containment, CORROSION/02, Paper No. 539 (Houston, TX: NACE International, 2002)
7. T. S. Summers, Aging and Thermal Stability of the Waste Package Outer Barrier, Report ANL-EBS-MD-000002 (Yucca Mountain Project, March 2000)
8. R. B. Rebak, T. S. Summers, and P. Crook, Effect of Thermal Stability on the Corrosion Behavior of Wrought and Welded Alloy 22, CORROSION/02, Paper No. 542 (Houston, TX: NACE International, 2002)

**TABLE 1 Composition of Alloys****Composition of Ni-Cr-Mo Alloys**

UNS No.	Alloy Name	Cr	Mo	W	Fe	Co	Mn	Si	C	P	S	Ni	Other
N06022	C-22	20.0-22.5	12.5-14.5	2.5-3.5	2.0-6.0	2.5 max	0.50 max	0.08 max	0.015 max	0.02 max	0.02 max	Rem	V: 0.35 max
N06455	C-4	14.0-18.0	14.0-17.0		3.0 max	2.0 max	1.0 max	0.08 max	0.015 max	0.04 max	0.03 max	Rem	Ti: 0.70 max
N10276	C-276	14.5-16.5	15.0-17.0	3.0-4.5	4.0-7.0	2.5 max	1.0 max	0.08 max	0.02 max	0.030 max	0.030 max	Rem	V: 0.35 max
N06059	59	22.0-24.0	15.0-16.5		1.5 max	0.3 max	0.5 max	0.010 max	0.010 max	0.015 max	0.010 max	Rem	Al: 0.1-0.4
N06686	686	19.0-23.0	15.0-17.0	3.0-4.4	5.0 max		0.75 max	0.08 max	0.010 max	0.04 max	0.02 max	Rem	

**Composition of Ti Alloys**

UNS No.	Grade	Intentional Elements	Residual Elements	Other
R52400	Grade 7	Pd: 0.12-0.25	C: 0.03 max; Fe: 0.30 max; H: 0.015 max; N: 0.03 max; O: 0.25 max	
R52402	Grade 16	Pd: 0.04-0.08	C: 0.10 max; Fe: 0.30 max; H: 0.010 max; N: 0.03 max; O: 0.25 max	Other residuals: each 0.1 max; total 0.4 max
R53400	Grade 12	Mo: 0.2-0.4; Ni: 0.6-0.9	C: 0.08 max; Fe: 0.30 max; H: 0.010 max; N: 0.03 max; N: 0.020 max; O: 0.25 max	

**TABLE 2. Nomenclature and Composition of Waters Used in Corrosion Testing**

Ion/Species	Simulated Dilute Water (SDW) (mg/L)	Simulated Concentrated Water (SCW) (mg/L)	Simulated Acidified Water (SAW) (mg/L)	Simulated Saturated Water (SSW) (mg/L)	Basic Saturated Water (BSW) (mg/L)
K <sup>+</sup>	34	3400	3400	141,600	67,620
Na <sup>+</sup>	409	40,900	37,690	48,700	105,840
Mg <sup>+2</sup>	1	1	1000	--	--
Ca <sup>+2</sup>	0.5	1	1000	--	--
F <sup>-</sup>	14	1400	--	--	1470
Cl <sup>-</sup>	67	6700	24,250	128,400	130,830
NO <sub>3</sub> <sup>-</sup>	64	6400	23,000	1,310,000	139,650
SO <sub>4</sub> <sup>-2</sup>	167	16,700	38,600	--	14,700
HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>-2</sup>	947	70,000	--	--	
Si	27 (60 C)/49 (90)	27 (60 C)/49 (90)	27 (60 C)/49 (90)	--	
pH (calculated)	8.1	8.1	2.7	7.0	11
pH (measured)	10.1	10.3	2.8	6.7	

**TABLE 3 – Compilation of General Corrosion Rates of Alloy 22 Specimens Exposed to SCW, SAW, and SDW at 60 and 90 C (Corrosion rates in nanometers/year)**

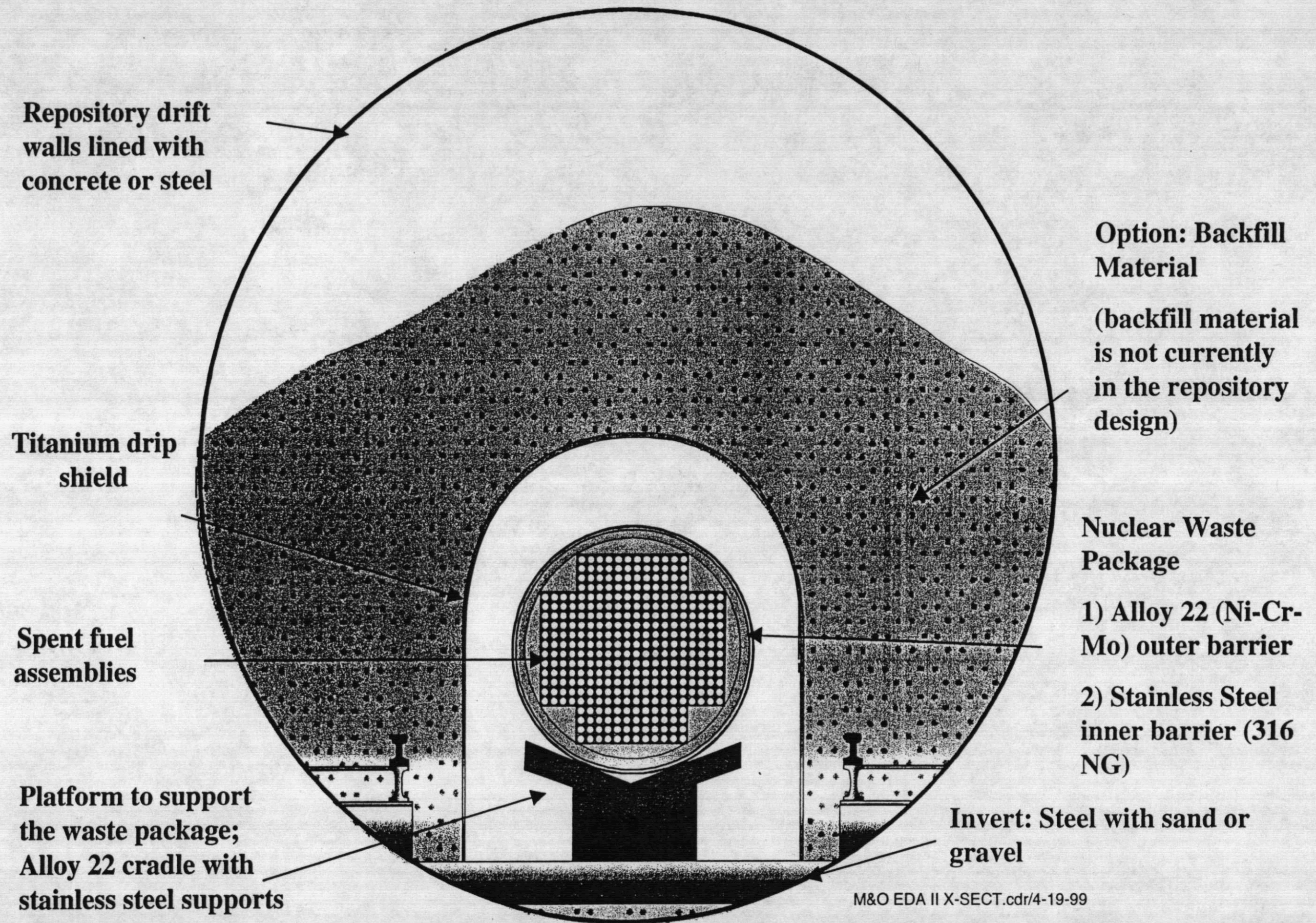
Exposure Interval	Mean (nanometers/year)	Range (nanometers/yr)	Remarks
6 months	50	-60 to +730	Negative value = weight gain even after cleaning
12 months	30	-40 to +100	
24 months	10	-30 to +70	

### List of Figures

1. Engineered Barrier Systems after Repository Closure
2. Cutaway of a Drift with Three Different Types of Waste Packages
3. Integrated Model for Waste Package and Drip Shield Performance

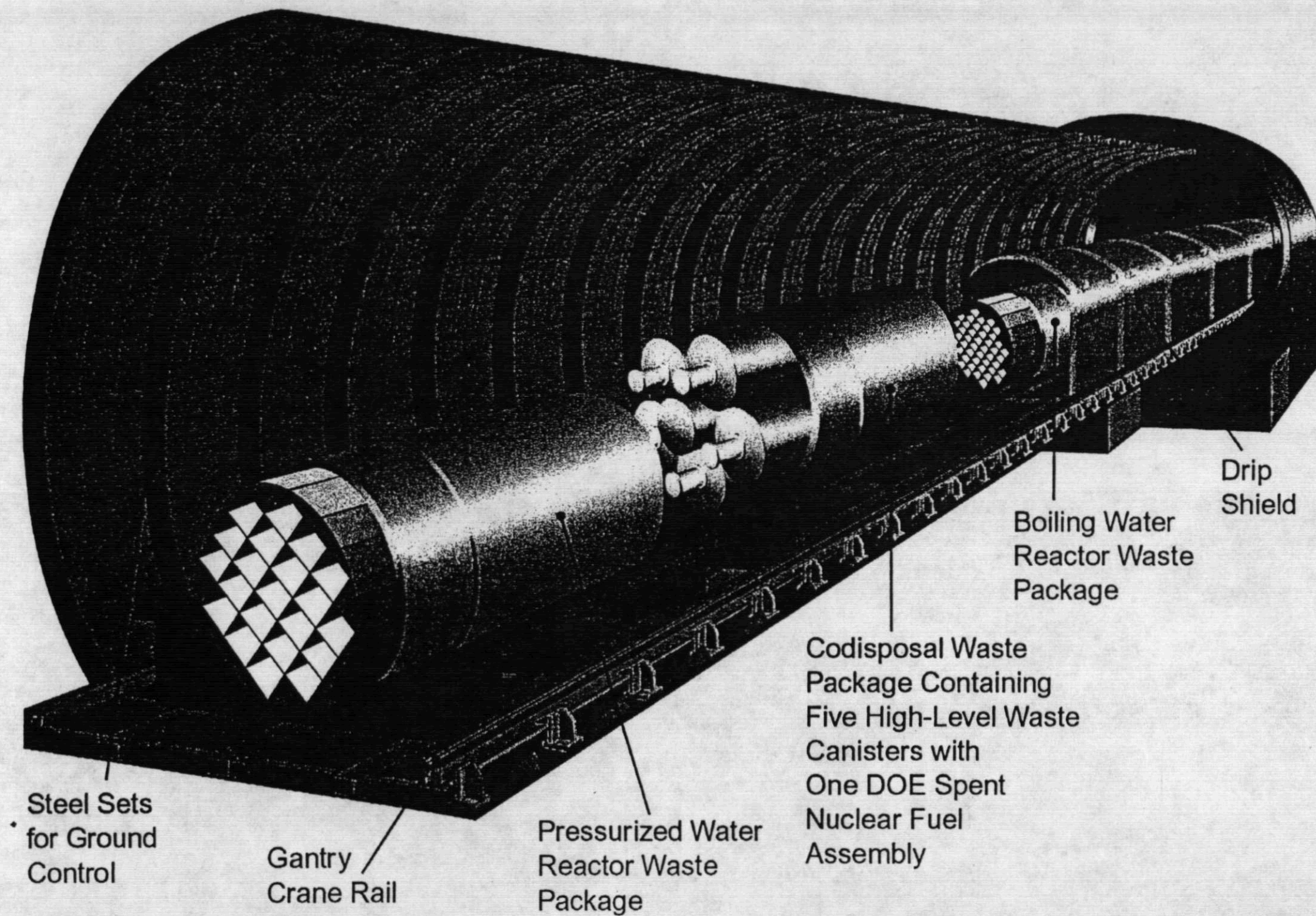


**Figure 1 -- Engineered Barrier System after Repository Closure**





# Figure 2 -- Cutaway of a Drift with Three Types of Waste Packages



Drawing Not to Scale  
00022DC-SRCR-V1S30-02c.ai



**FIGURE 3 Integrated Model for Waste Package and Drip Shield Performance**

